NANOSTRUCTURED Pt/MnO_2 CATALYSTS AND THEIR PERFORMANCE FOR OXYGEN REDUCTION REACTION IN AIR CATHODE MICROBIAL FUEL CELL

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ABSTRACT

Microbial fuel cells (MFCs) represent a promising sustainable clean technology for simultaneous bioelectricity generation and wastewater treatment. Catalysts are significant portions of the cost of microbial fuel cell cathodes. Many materials have been tested as aqueous cathodes, but air-cathodes are needed to avoid energy demands for water aeration. The sluggish oxygen reduction reaction (ORR) rate at air cathode necessitates efficient electrocatalyst such as carbon supported platinum catalyst (Pt/C) which is very costly. Manganese oxide (MnO_2) was a representative metal oxide which has been studied as a promising alternative electrocatalyst for ORR and has been tested in air-cathode MFCs. However the single MnO_2 has poor electric conductivity and low stability. In the present work, the MnO_2 catalyst has been modified by doping Pt nanoparticle. The goal of the work was to improve the performance of the MFC with minimum Pt loading. MnO_2 and Pt nanoparticles were prepared by hydrothermal and sol gel methods, respectively. Wet impregnation method was used to synthesize Pt/MnO_2 catalyst. The catalysts were further used as cathode catalysts in air-cathode cubic MFCs, in which anaerobic sludge was inoculated as biocatalysts and palm oil mill effluent (POME) was used as the substrate in the anode chamber. The as-prepared Pt/MnO_2 was characterized comprehensively through field emission scanning electron microscope (FESEM), X-Ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry (CV) where its surface morphology, crystallinity, oxidation state and electrochemical activity were examined, respectively. XPS revealed Mn (IV) oxidation state and Pt (0) nanoparticle metal, indicating the presence of MnO_2 and Pt. Morphology of Pt/MnO_2 observed from FESEM shows that the doping of Pt change the urchin-like structure of MnO_2 into cocoon-like structure of Pt/MnO_2. The electrochemical active area of the Pt/MnO_2 catalysts has been increased from 276 to 617 m^2/g with the increase in Pt loading from 0.2 to 0.8 wt%. The CV results in O_2 saturated neutral Na_2SO_4 solution showed that MnO_2 and Pt/MnO_2 catalysts could catalyze ORR with different catalytic activities. MFC with Pt/MnO_2 (0.4 wt% Pt) as air cathode catalyst generates a maximum power density of 165 mW/m^3, which is higher than that of MFC with MnO_2 catalyst (95 mW/m^3). There was a slight increase in COD removal efficiency of 0.4 wt% Pt/MnO_2 (84%) compared to MnO_2 and other Pt loading catalysts. The open circuit voltage (OCV) of the MFC operated with MnO_2 cathode gradually decreased during 14 days of operation, whereas the MFC with Pt/MnO_2 cathode remained almost constant throughout the operation suggesting the higher stability of the Pt/MnO_2 catalyst. Therefore, Pt/MnO_2 with 0.4 wt% Pt successfully demonstrated as an efficient and low cost electrocatalyst for ORR in air cathode MFC with higher electrochemical activity, stability and hence enhanced performance as well as higher COD removal efficiency.

ABSTRAK

Sel-sel bahan api mikrob (MFCs) merupakan teknologi yang berpotensi untuk tujuan generasi bioelektrik dan rawatan air sisa serentak. Pemangkin adalah bahagian penting daripada kos katod sel bahan api mikrob. Banyak bahan telah diuji sebagai katod akueus, tetapi katod udara diperlukan bagi mengelakkan penggunaan tenaga untuk pengudaraan air. Kadar reaksi pengurangan oksigen (ORR) yang lembap di katod udara memerlukan pemangkin cekap seperti pemangkin platinum disokong karbon (Pt/C) yang amat mahal. Mangan oksida (MnO_2) adalah oksida logam yang telah dikaji sebagai pemangkin alternatif untuk ORR dan telah diuji dalam MFCs katod udara. Namun MnO_2 mempunyai kekonduksian elektrik yang lemah dan kestabilan yang rendah. Dalam karya ini, pemangkin MnO_2 telah diubah suai dengan menaburkan Pt nanopartikel. Matlamat kerja ini adalah untuk meningkatkan prestasi MFC dengan minimum kandungan Pt. MnO_2 dan Pt nanopartikel telah disediakan melalui kaedah hidroterma dan sol gel masing-masing. Kaedah pengisitepuan basah telah digunakan untuk mensintesis pemangkin Pt/MnO_2. Pemangkin digunakan sebagai pemangkin katod di katod udara MFCs padu, di mana enapcemar anaerobik telah disuntik sebagai pemangkin biologi dan bahan buangan kilang minyak sawit (POME) sebagai substrat dalam kebuk anod. Pt/MnO_2 yang disediakan dicirikan secara komprehensif melalui bidang pelepasan mikroskop imbasan elektron (FESEM), X-Ray pembelauan (XRD), sinar-X fotoelektron spektroskopi (XPS), dan voltammetri berkitar (CV) di mana morfologi permukaannya, penghabluran, pengoksidaan dan aktiviti elektrokimia telah diperiksa, masing-masing. XPS mendedahkan Mn (IV) pengoksidaan dan Pt (0) nanopartikel logam, menunjukkan kewujupan MnO_2 dan Pt. Morfologi Pt/MnO_2 yang diperhatikan dari FESEM menunjukkan bahawa penaburan Pt menyebabkan perubahan struktur urchin MnO_2 kepada struktur cocoon Pt/MnO_2. Kawasan aktif elektrokimia pemangkin Pt/MnO_2 telah meningkat dari 276 kepada 617 m^2/g dengan peningkatan dalam kandungan Pt 0.2-0.8 wt%. Peningkatan dalam keberkesanan peningkiran COD diperhatikan pada 0.4 wt% Pt/MnO_2. Keputusan CV menggunakan larutan neutral Na_2SO_4 tepu dengan O_2 menunjukkan pemangkin MnO_2 dan Pt/MnO_2 boleh menjadi pemangkin ORR dengan aktiviti-aktiviti pemangkin yang berbeza. MFC dengan Pt/MnO_2 (0.4 wt% Pt) sebagai pemangkin katod udara menjana ketumpatan kuasa maksimum 165 mW/m^3, iaitu lebih tinggi daripada MFC dengan MnO_2 pemangkin (95 mW/m^3). Voltan litar terbuka (OCV) daripada MFC dikendalikan dengan MnO_2 katod menurun secara beransur-ansur dalam 14 hari beroperasi, manakala MFC dengan Pt/MnO_2 katod yang kekal hampir malar sepanjang operasi itu mencadangkan kestabilan yang lebih tinggi oleh pemangkin Pt/MnO_2. Oleh itu, Pt/MnO_2 dengan 0.4 wt% Pt berjaya menunjukkan ia sebagai pemangkin cekap yang berkos rendah untuk ORR di katod udara MFC dengan aktiviti elektrokimia dan kestabilan yang lebih tinggi, justeru prestasi yang dipertingkatkan serta peningkiran COD yang lebih tinggi.

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I	current
V	voltage
P	power
R	resistance
V	volume

Greek

Ω	ohm (resistance)

LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
COD	Chemical oxygen demand
CV	Cyclic voltammetry
DI	Deionised water
EIS	Electrochemical impedance spectroscopy
FESEM	Field emission scanning electron microscope
MEA	Membrane electrode assembly
MFC	Microbial fuel cell
ORR	Oxygen reduction reaction
PACF	Polyacrylonitrile carbon felt
PEM	Proton exchange membrane
POME	Palm oil mill effluent
TEM	Transmission electron microscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

1 INTRODUCTION

1.1 Chapter Overview

In this chapter of introduction, background of study, problem statement and motivation, objective, scopes of study as well as significance of work will be presented.

1.2 Background

The major global concerns of present time are energy crisis and wastewater treatment which have triggered growing awareness. For decades, there has been heavy dependence on fossil fuels of finite supply for energy harvesting purpose. Natural gas, crude oil, and coal, for instance, are being exploited in large extent in order to meet the global massive energy demand. Undoubtedly, due to rapid advancement in civilization, energy demand of mammoth capacity is constantly on the rise. Global energy demand is expected to project to 27 TW by 2050 and 43 TW by 2100 (Lewis and Nocera, 2006). According to US Energy Information Administration (2010), the total world energy demand is around 510 quadrillion BTUs, of which approximately 450 quadrillion BTUs (88%) of world energy is derived from depleting fossil fuels which are on the brink of exhaustion. It has been estimated that the current reservoir of fossil fuels can last for another 104 years if the world consumption of renewable energy sources remains constant (US Department of Energy, 2011). There is a sheer of nearly 7% of energy needs is supplied from renewable energy resources such as solar energy, wind and hydroelectric power. Furthermore, nuclear energy, a controversial and non-renewable energy resource provides only around 5% of the world's energy supplies (Energy Information Administration, 2010). Due to public pressure and relative dangers associated with harvesting energy from atom, nuclear energy is not likely to be a major source of world energy consumption. Practically, nearly all the existing conventional energy generation technologies which require combustion of fossil fuels are cost ineffective and non-environmental friendly because of the emission of carbon dioxide (CO_2). Concentration of greenhouse gas, CO_2 is estimated will reach from 540 to 970ppmv by 2100 (Logan, 2008). This will certainly exacerbate environmental damage besides accelerate global climate change. On the account of fossil fuels' unsustainability

and polluting nature, there is an urgent and indispensable need for the searching of viable alternatives as the sustainable new renewable energy resources to resolve the critical twins problems.

Moreover, in line with the rapid development of country has inevitably contributed to the generation of huge amount of wastewater from a variety of industries. Substantial amount of energy is needed for the implementation of conventional wastewater treatment technologies. This can be exemplified in United States where an estimated 1.5% of the total electricity produced is utilized for wastewater treatment solely, and approximately 4-5% of the electrical energy is used for the whole water infrastructures (Logan, 2008). The high energy requirement has been the constant concern which critically needs promising alternative to resolve.

The discovery that microbial metabolism could provide energy in the form of electrical current has led to an increasing interest in the field of MFCs research (Allen and Bennetto, 1993). Microbial fuel cells (MFCs) represent a novel and sustainable promising technology for the simultaneous bioelectricity generation from biomass using bacteria and wastewater treatment (Logan, 2008). The main advantage of MFC technology is direct electricity generation from low grade substrates with net zero consumption of fossil fuels (Logan, 2008). The nature of substrate used as source of energy in the anode of MFC significantly affects the electricity production (Pant et al., 2010). A broad spectrum of substrates can be used in MFCs for the generation of electricity. Rabaey et al. (2003) demonstrated with success that the use of glucose as substrate in MFC is possible by generating power density two orders of magnitude greater. Apart from pure substrates like glucose and acetate, wastewater is one of the promising complex substrates as it contains various kinds of organic matters, including carbohydrate, protein, nitrogenous materials and minerals. Domestic and industrial wastewaters instead of pure substrates have been extensively studied well in recent years, swine wastewater, paper recycling plant waste, and starch processing wastewater, to name a few (Oh and Logan, 2005; Lu et al., 2009; Wang et al., 2009; Wen et al., 2009). Palm oil mill effluent (POME) is an organic industrial wastewater produced from oil palm processing plant.

Malaysia is the largest producer of palm oil globally with 49.5% of world production (Wu et al., 2008). In Malaysia, the abundance of oil palm processing industries has

contributed to the generation of substantial amount of POME. Around 3 tonnes of POME is generated with every tonne of crude palm oil produced (Ahmad et al., 2003). The existing POME treatment technologies such as anaerobic biological processes (Edewor, 1986), chemical coagulation and flotation (Badri, 1984; Chin et al., 1987; Ho and Chan, 1986), land disposal (Ma and Ong, 1986), simple skimming devices (Roge and Velayuthan, 1981), and aerobic (Abdul et al., 1989) are inefficient as they are highly energy intensive, aerobic treatment, in particular (Pham et al, 2006; Pant et al, 2007). High cost incurred for high energy supply. The major operating costs for wastewater treatment constitute of wastewater pumping, sludge treatment and wastewater aeration where half of the operation costs are contributed by aeration alone. In order to make it energy efficient, POME has recently been investigated as a potential substrate in MFC by Baranitharan and coworkers (2013). In their study, a two-chamber MFC was used and it was found that the low strength (low Chemical Oxygen Demand, COD) POME is preferable in order to achieve high efficiency in the MFC. In the two-chamber MFC, the catholyte is usually potassium permanganate solution ($KMnO_4$) and it requires extra space to operate.

Air cathode MFCs are a variation of MFCs where the cathode compartment is exposed to the air. Oxygen is the most ideal electron acceptor due to its cost effectiveness, high redox potential and sustainability comparing with many types of electron acceptors that can be used in MFC (Logan, 2008; Zhang et al., 2011). In the air-cathode MFC, due to the reduction of molecular oxygen (O_2) in cathode, it is the best choice for both chemical fuel cells and for MFCs, because the reduction product is clean and non-polluting water (H_2O). Oxygen reduction reaction (ORR) typically requires electrocatalyst for its sluggish rate. Hence, the type of electrocatalyst is vital in influencing the performance of MFCs (Cheng et al., 2006).

1.3 Problem Statement and Motivation

The driving forces which lead to the decision of developing nanostructured platinum doped manganese dioxide electrocatalyst (Pt/MnO_2) are attributed by several factors. Platinum is a well-known novel candidate of electrocatalyst which has demonstrated high electrocatalytic activity and stability for oxygen reduction reaction (ORR) in air cathode microbial fuel cell (MFC) (Steele and Heinzel, 2001).). For instances, platinum supported on carbon (Pt/C) is the common efficient catalyst used for ORR but its

application is limited due to high cost (Bashyam and Zelenay, 2006; Yu et al., 2007). Alternatively, efforts in the search for low cost catalysts are on the way. A large number of low cost catalysts have been investigated as alternatives without compromising its performance in air cathode MFC. These include macrocycle material (Zhao et al., 2005), metal porphyrins (HaoYu et al., 2007), iron phthalocyanine (Birry et al., 2011; Yuan et al., 2011; Yuan et al., 2010; Zhao et al., 2005), lead dioxide (Morris et al., 2007), Co/Fe/N/CNT (Deng et al., 2010), iron-chelated ethylenediaminetetraacetic acid (et al., 2011), nickel powder (Zhang et al., 2009), Co-naphthalocyanine (et al., 2007) and metal oxides (Morris et al., 2007). Unfortunately, these alternative catalysts have been proven as non-effective due to the long term instability (ter Heijne et al., 2007).

Non-noble catalyst, manganese dioxide (MnO_2) is among metal oxides which has been well studied and tested in air-cathode MFC recently (Cheng et al., 2010; Gong et al., 2007; Li et al., 2010; Roche et al., 2010; Roche and Scott, 2009; Zhang et al., 2009). MnO_2 exhibits advantages of low cost, environmental friendliness and high catalytic activity. Clauwaert et al. (2007) and Roche and Scott (2010) have investigated MnO_2 in neutral medium (pH 7) where it has been determined as efficient ORR catalyst. Zhang and coworkers have reported the use of MnO_2 in MFC where β-MnO_2/graphite was the efficient catalyst for ORR (2009). Furthermore, in the same year of 2010, Roche et al. used MnO_2 supported on carbon whereas Liu et al. employed single MnO_2 without catalyst support generated power density of 161 mW/m^2 and 772.8 mW/m^3, respectively. Despite of the fact that good performance been observed through these studies, stability issue found in MnO_2 was the hindrance to its widespread application in MFC. According to Hou et al., the single MnO_2 has intrinsically poor electrical conductivity and low stability. Moreover, due to its dense morphology, electrochemical performance of MnO_2 alone is not optimistic (2010).

With the aims of improving stability, electrochemical activity and hence improved MFC performance, doping of novel metals, such as platinum (Pt) or gold (Au) is believed to be able to improve the stability and performance of the catalysts. Doping of novel metals, such as Pt or Au nanoparticles (NPs) on supports has many advantages. These include increasing the number of surface atoms and hence active sites, consequently bringing synergistic effects between support and NPs, apart from lowering the cost ofcatalysts (Yu et al., 2012). The control of the novel metal loading is a critical issue

for electrocatalyst synthesis. Herein, in the present work, the MnO_2 catalyst has been modified by doping Pt NPs. The goal of the work was to improve the performance of the MFC using nanostructured Pt/MnO_2 with minimum Pt loading without compromising the low cost aimed.

1.4 Objective

The objective of the present work is to synthesize and characterize nanostructured platinum doped manganese dioxide (Pt/MnO_2) electrocatalyst as well as to investigate the performance of the electrocatalysts in air cathode microbial fuel cell (MFC) for the simultaneous electricity generation and treatment of palm oil mill effluent (POME).

1.5 Scope of Study

The scopes of the present work are to synthesize nanostructured platinum doped manganese dioxide (Pt/MnO_2) air cathode electrocatalyst by wet impregnation method from pre-synthesized platinum (Pt) nanoparticles (NPs) by sol gel method and pre-synthesized manganese dioxide (MnO_2) nanoparticles by hydrothermal method. Secondly, to characterize comprehensively electrocatalysts synthesized by field emission scanning electron microscope (FESEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry (CV). Third, to fabricate membrane-electrode-assembly (MEA) by coating catalyst with Nafion solution onto carbon felt followed by hot pressing with pre-treated Nafion membrane. Lastly, performance of electrocatalyst in air cathode microbial fuel cell will be evaluated in terms of open circuit voltage (V), volumetric power density (W/m^3), and chemical oxygen demand (COD) removal efficiency.

1.6 Significance of Study

The implications of present work to society as well as environment are apparent. With the utilization of Pt/MnO_2 in air cathode microbial fuel cell (MFC) which will yield better performance and higher COD removal efficiency, its implementation in industrial sector, particularly in wastewater treatment plant will have a large degree of positive effect. For example, the electricity required for the treatment plant will be reduced which consequently reducing the operating cost apart from having net zero emission of greenhouse gases, CO_2 to the atmosphere by harvesting energy from MFC instead of

carbon sources such as fossil fuels which are of polluting nature. In addition to power generation, the treatment of waste water will be achieved to a certain degree with the degradation of organic and inorganic matter by microorganisms.

1.7 Organisation of Thesis

The structure of the remaining of the thesis is outlined as follow:

Chapter 2 provides a view of the related literature done on present work from a wide variety of spectrums. General descriptions on the working principle, configurations as well as advantages of microbial fuel cells are presented. Besides, parameters affecting the performance of microbial fuel cell are being discussed. In addition, a brief discussion of the mechanisms of oxygen reduction reaction and hence requirement for electrocatalysts is performed. Works from literature which lead to the development of the objective of current work also being discussed where a summary of the literature review is presented at the end of chapter.

Chapter 3 gives a detailed step-by-step description of the experimental works performed in the execution of the current work along with graphical aids. Besides, comprehensive analysis and characterization performed also been outlined.

Chapter 4 is devoted to the detailed and in-depth discussion of the results of characterization and analysis conducted. In addition, evidences as well as justification on any discrepancies or similarities supported with existing works are presented. Enlightening information and knowledge related to present work are provided as well in this chapter. Eventually, it revealed all the unknowns after the commencement of the experiment.

Chapter 5 draws together a summary of the thesis and outlines the future work which might be beneficial to the further development and improvement on current work.

2 LITERATURE REVIEW

2.1 Chapter Overview

Chapter 2 outlined the literature studies related to the present work. These include power generation by microbial fuel cells and its present status, factors affecting microbial fuel cell performance, air cathode microbial fuel cell, cathodic limitations of air cathode microbial fuel cell, ohmic losses, mass transport losses, activation overpotential, oxygen reduction reaction, platinum-based electrocatalysts, non-platinum based electrocatalysts, performance of non-platinum electrocatalysts, oxygen reduction reaction pathway on manganese oxides, limitations of manganese dioxide in air cathode microbial fuel cell, modification of manganese dioxide as well as the summary of all the literature review done.

2.2 Power Generation by Microbial Fuel Cells and Its Present Status

Fuel cell is a technology which has been employed as an alternative energy resource in field like transportation, portable power, and electric utility. By far, several types of fuel cell have already been developed and introduced for utilization. For examples, proton exchange membrane fuel cells (PEMFC), alkaline fuel cells (AFC), phosphoric acid fuel cells (PAFC), molten carbonate fuel cells (MCFC), solid oxide fuel cells (SOFC), direct formic acid fuel cells (DFAFC), direct methanol fuel cells (DMFC), and microbial fuel cells (MFCs) (Holland, 2007; Leong et al., 2013; Schroder, 2007).

Microbial fuel cells (MFCs) are one of the variations of bioelectrochemical fuel cells other than enzymatic fuel cells. It involves the conversion of chemical energy to electrical energy by exploiting biological components. It is a promising bioenergy technology whereby electrochemically active microorganisms, acting as biocatalyst is used to decompose a broad spectrum of organic and inorganic matters at anode through microbial respiration and electricity is harvested simultaneously (Rabaey and Verstraete, 2005; Allen and Bennetto, 1993). Microbial fuel cell commonly consists of an anode and a cathode, which separates by solid electrolyte bridge like proton exchange membrane or connected directly to wastewater substrate (Leong et al., 2013). During degradation process under anaerobic condition at the anode chamber of MFCs,

carbon dioxide, protons and electrons will be produced. The electrons and protons produced will migrate through electric circuit and membrane separator (if any), respectively and combine together with oxygen molecule at cathode to form water molecule. The typical reactions occurred at the anode (oxidation) and cathode (reduction) are presented in the equations as shown below (Liu, 2004).

Anode: $C_xH_yO_z + H_2O \rightarrow CO_2 + e^- + H^+$ (2-1)

Cathode: $O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$ (2-2)

The overall reaction is the degradation of the substrate to carbon dioxide and water with a concomitant production of electricity.

The development of MFCs can be dated back to nearly 100 years ago. As reported by Potter (1911), he concluded that electric energy can be harvested from the microbial degradation of organic matters. In year 1931, Cohen confirmed the results reported by Potter and recorded a stacked bacterial fuel cell yielding voltage and current of 35 V and 0.2 mA, respectively. In addition, according to Suzuki (1976), microbes used as biocatalyst in MFCs was explored from the 1970s whereas the application of MFCs in wastewater treatment were reported in year 1991 (Habermann and Pommer, 1991). However, there was low power production and the impact of MFCs employed on treated wastewater's strength was unknown. It was then that in year 2004, Liu and coworkers discovered the link between the power generated using MFCs and wastewater treatment was forged as in their work domestic wastewater used could be treated to practical levels and at the same time generating electricity. MFCs are hence been developed providing possible chances for practical applications (Liu and Logan, 2004).

Various configurations of MFCs have been developed over the years, for instances, double chamber MFCs, single chamber MFCs, plate MFCs, stacked MFCs and tubular MFCs, with single and double chamber MFCs being the more common ones. The anode and the cathode of a double chamber MFC are placed in two distinct compartments where they are partitioned by a proton exchange membrane. On the contrary, the cathode of a single chamber MFC is directly exposed to the air, leaving the MFC with only a single anode chamber (Pandey et al., 2011). On the other hand, tubular MFCs have a cylindrical or tubular shape where the cathode is exposed to the air while the

membrane-electrode-assembly (MEA) is wrapped around a central anode chamber (Kim et al., 2009). In plate type MFCs having a flat rectangular shape, the MEA is sandwiched between two non-conductive rectangular plates where their inner surfaces etched with flow channels that allow wastewater to flow at the anode and air to flow at the cathode (Min and Logan, 2004).Whereas for stack MFCs, they are used for the purpose of scaling up by arranging them in a stack, either in series or in parallel, in order to generate higher voltage or larger current densities, respectively (Aelterman et al., 2006). Figures below depict different types of MFCs.

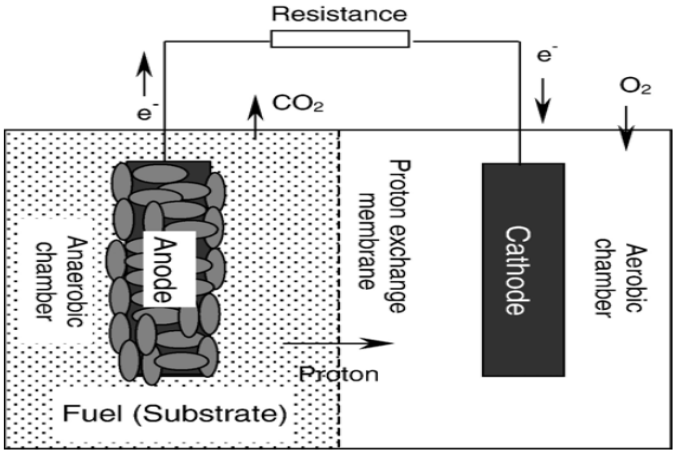

Figure 2-1:Schematic diagram of a double chamber microbial fuel cell (Du et al, 2007)

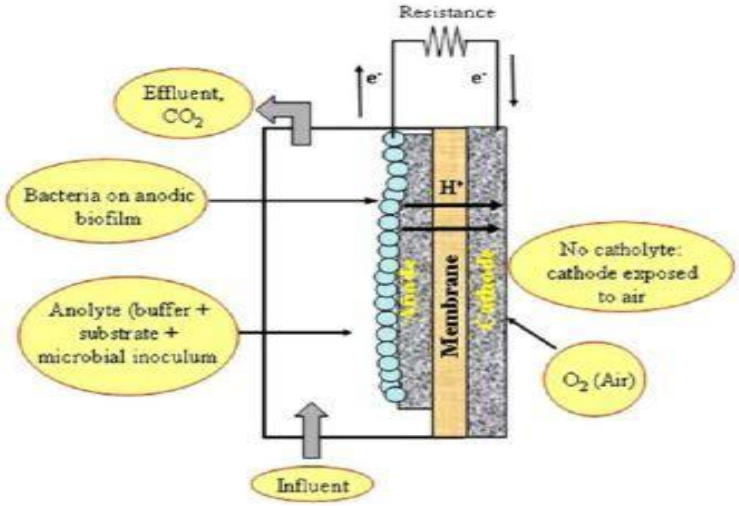

Figure 2-2: Schematic diagram of a single chamber microbial fuel cell (Du et al., 2007)

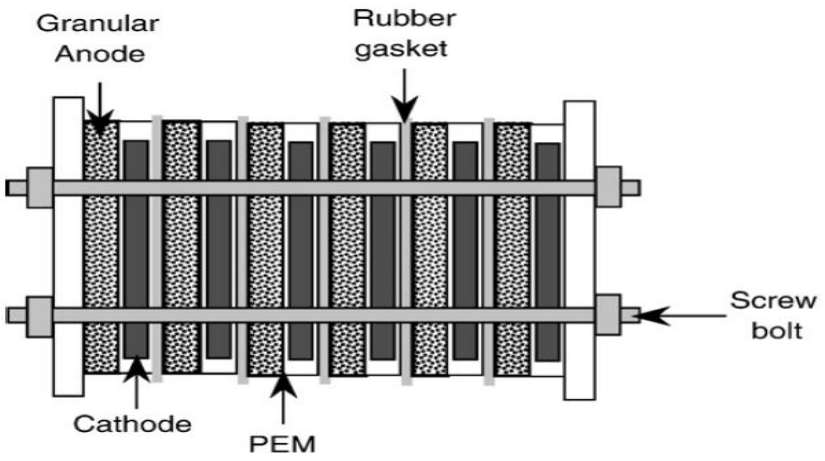

Figure 2-3: Stacked microbial fuel cells consisting of six individual units with granular graphite anode (Du et al., 2007)

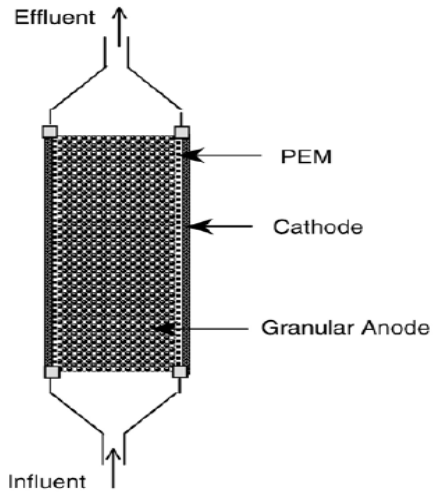

Figure 2-4: Tubular microbial fuel cell with outer cathode and inner anode consisting of graphite granules (Du et al., 2007)

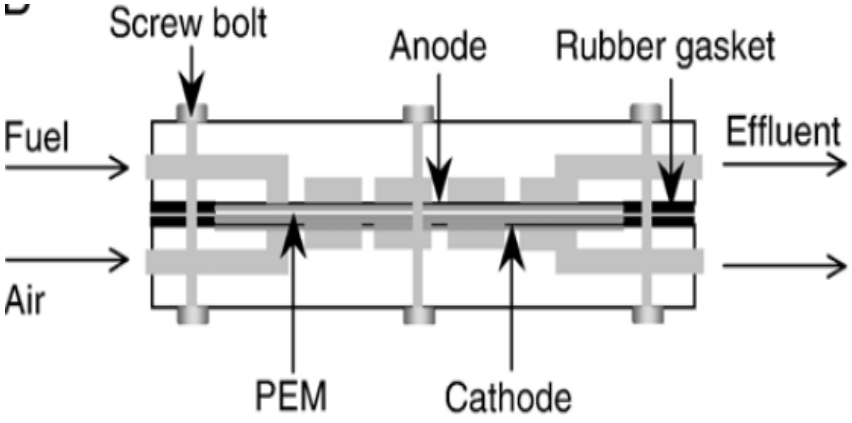

Figure 2-5: Schematic of a flat type microbial fuel cell (Du et al., 2007)

Table 2.1 shows the example of basic components of microbial fuel cells

Table 2-1: Basic components of microbial fuel cells

Items	Materials	Remarks
Anode	Graphite, graphite felt, carbon paper, carbon cloth,	Necessary
Cathode	Graphite, graphite felt, carbon paper, carbon cloth	Necessary
Anodic chamber	Glass, polycarbonate, plexiglass	Necessary
Cathodic chamber	Glass, polycarbonate, plexiglass	Optional
Proton exchange system	Proton exchange membrane: Nafion, ultrex, polyethylene, salt bridge	Necessary
Electrode catalyst	Pt, Pt black, MnO_2	Optional

(Source: Du et al., 2007)

MFCs exhibit key advantages over technologies currently used for producing electricity utilizing organic matter. First and foremost, high conversion efficiency is ensured in the direct conversion of substrate energy to electricity. Besides, gas treatment is not required in MFCs as off-gases of MFCs are enriched in carbon dioxide (CO_2) and have no useful energy content. Moreover, MFCs can operate at ambient and even at low temperature which differentiating them from the current bioenergy processes. In addition, there is no energy requirement for aeration whereby the cathode is passively aerated in MFCs (Liu et al., 2004). This is the notable feature exhibited by MFCs as aeration alone can account for half of the operation costs at a typical treatment plant (Logan, 2008). At last, MFCs is a promising technology for widespread application in places lacking of electrical infrastructures and as the alleviation to the energy crisis currently being encountered by expanding the diversity of energy resources (Rabaey and Verstraete, 2005).

The present status of power generation by MFCs is presented in Figure 2.6. It can be seen that given the low working volume of MFCs, higher power density is generated than the high volume systems. In the range of 10 to 100 mL, the maximum power generation achieved was in the range of 100 to 500 W/m^3. Looking at the types of substrates used as shown in Figure 2.7, the power generated by MFCs dropped from

that using simple substrate such as glucose (100 W/m^3) to 10 W/m^3 of that with complex substrate like industrial wastewater.

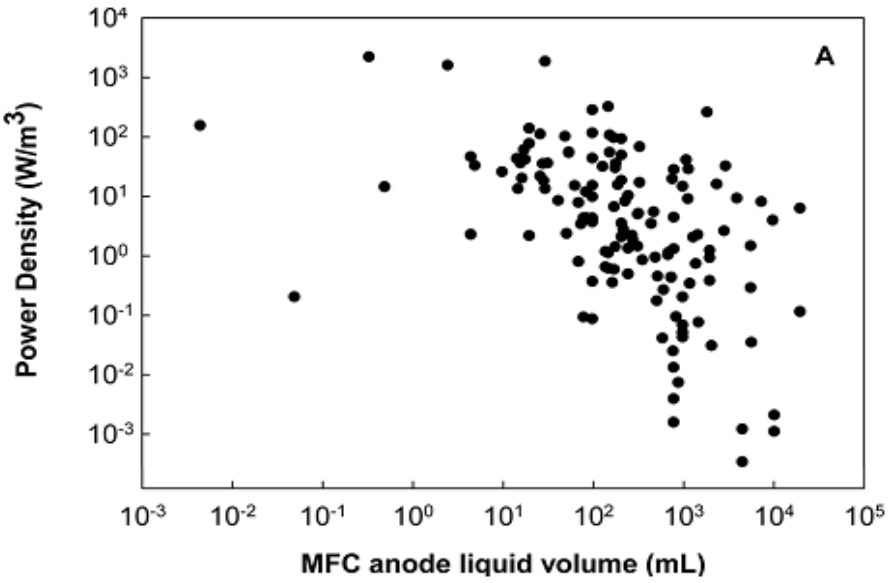

Figure 2-6: Electricity generation in microbial fuel cells with different anode liquid volumes (Ge et al., 2012)

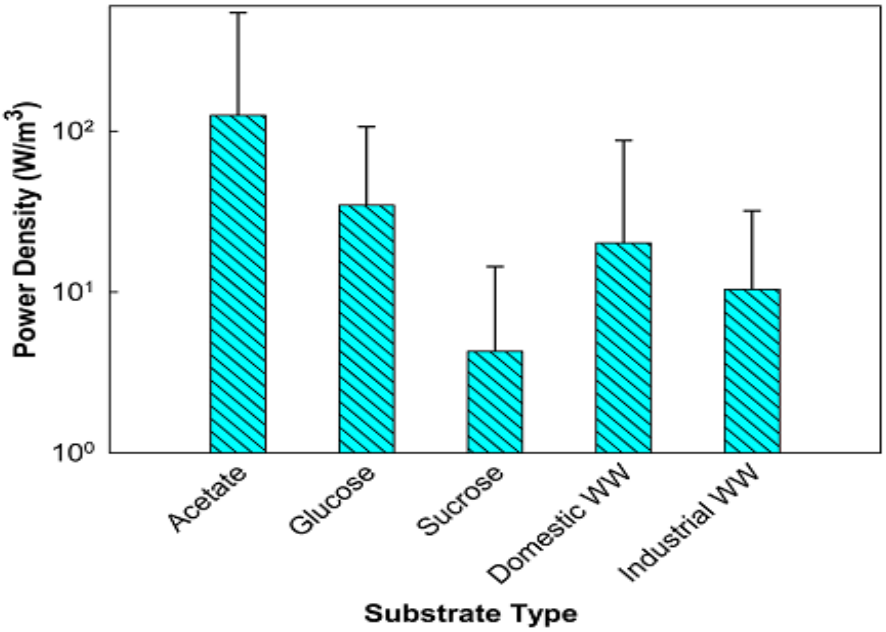

Figure 2-7:Power density by microbial fuel cells treating different types of substrates (Ge et al., 2012)

Garnering knowledge on MFCs is essential for optimizing energy production from MFCs and future development of it.

2.3 Factors Influencing Microbial Fuel Cell Performance

To access the performance of MFCs, it depends on a complex system of parameters including types and concentrations of substrate, types of inoculum, pH of substrate, conductivity, microbial activity, circuit resistance, electrode material, electrocatalyst, and membrane material (Liu et al., 2005).

2.3.1 Microbial Metabolism

According to Schroder (2007), energy efficiency of MFCs is associated with the mechanisms of electron transfer occurred in anode of MFCs. In other words, the exploitation of every living cell to dispose the electrons liberated during substrate disintegration is the basis to the mechanism of microbes' metabolism. Metabolic routes governing proton flows as well as microbial electron. The electrons to be delivered towards the electrode need a physical transport system for extracellular electron transfer. According to Delaney et al. (1984), that can be happened through the use of soluble electron shuttles or through membrane-bound electron shuttling compounds (Vandevivere and Verstraete, 2001). On the other hand, the anode potential will determine the bacterial metabolism, subsequently redox potential of the final bacterial electron shuttle and hence metabolism. A number of different metabolism pathways can be classified based on the anode potential including fermentation, high redox oxidative metabolism, and medium to low redox oxidative metabolism. Microbes used in MFCs reported to date comprises of aerobes, facultative anaerobes and strict anaerobes (Rabaey and Verstraete, 2005). Table 2.2 summarized the kind of microbes used in MFCs.

Table 2-2: Summary of microbes used in microbial fuel cell

Microbes	Substrates	Applications	Reference
Actinobacillus succinogenes	Glucose	Electron mediator	Park and Zeikus, 2000
Aeromonas hydrophila	Acetate	Mediator-less MFC	Pham et al., 2003
Pseudomonas	Glucose	Self-mediate consortia isolated	Rabaey (2004)

aeruginosa		from MFC	
Clostridium beijerinckii	Starch	Fermentative bacterium	Niessen et al. (2004b)
Desulfovibrio desulfuricans	Sucrose	Sulphate/sulphide as mediator	Park et al., 1997)
Geobacter metallireducens	Acetate	Mediator-less MFC	Min et al. (2005a)
Rhodoferax ferrireducens	sucrose, maltose	Mediator-less MFC	Liu et al., 2006)

2.3.2 Types of Substrates

Apart from microbial metabolism, substrate is regarded as one of the prime factors affecting MFC power generation (Liu et al., 2009). Substrate serves as carbon or nutrient and energy source. According to Angenent and Wrennn, efficiency of converting organic wastes to bioenergy depends on the chemical compositions as well as concentrations of the components of waste material (2008). A broad spectrum of substrates can be used in MFCs system for power generation ranging from pure compounds such as glucose and organic acids, acetate, to complex mixtures of organic matter present in industrial, domestic, and animal waste wastewater.

Acetate, being the simple substrate (Bond et al, 2002), has been utilized extensively as the recalcitrance of multitude kinds of wastewater making them more difficult to be used as substrate for electricity generation (Sun et al., 2009b). Besides, acetate is inert towards alternative microbial conversions like fermentations and methanogenesis at room temperature (Aelterman, 2009). Chae et el. demonstrated that MFCs fed with acetate showed the highest CE (72.3%), followed by butyrate, propionate, and glucose with readings of 43.0%, 36.0% and 15.0%, respectively (2009).

Another commonly used substrate in MFCs is glucose. A maximum power density of 216 W/m^3 was obtained from a glucose-fed batch MFC using 100 mM ferric cyanide as cathode oxidant (Rabaey et al., 2003). As reported by Hu (2008), a maximum power of 161 mW/m^2 was generated in a baffle-chamber membraneless MFC inoculated with anaerobic sludge and glucose.